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Specification

1. Title of Invention

Rubber composition for tire tread.

2. Scope of Patent Claim

The rubber composition for tire treads comprising 10-50 weight parts of natural rubber and/or synthetic polyisoprene rubber and 50-90 weight parts of polyisoprene rubber with a polybutadiene rubber content of 50 wt% or more in which the content of trans 1-4 bonds is 30 wt% or more and the content of vinyl bonds is 10% or less, said composition characterized by the fact that 20-200 weight parts of carbon black are blended per 100 weight parts of said rubber and by the fact that the relation between the amount of dibutyl phthalate oil absorption x (ml/100 g) and the amount of iodine adhesion y (mg/g) by said carbon black satisfies relations Φ - Φ below

$-x + 110 \le y \le -x + 170$		 	 4
x ≤ 50	2.3		2
y ≤ 20			₫

3. Detailed Description of the Invention

This invention relates to a rubber composition for tire treads. Specifically, it concerns a rubber composition for tire treads used in steel-belted radial tires for passenger cars comprising natural rubber and/or synthetic polyisoprene rubber and polybutadiene rubber in which specific polybutadiene rubber is the main component of the raw material rubber ingredient in which the braking performance on wet, snow-packed and icy road surfaces has been improved by the blending of carbon black having specific properties.

Studded tires or chains have been used in the past to run on packed snow-icy roads (hereinafter termed icy surfaces). However, such studded tires or chains have not been suitable for use on high-speed roads in cold regions or high-speed roads traversing mountains or forests where there are occasional tcy sections. The use of such studded tires or chains on roads which are not covered by ice diminishes the steering stability, running stability and they damage the road surface. It is essential that such studded tires be replaced by normal tires, or that chains be removed for use on high-speed roads. Furthermore, icy sections turn into wet pavement during the day, and such wet pavement also poses safety problems for such tires. A tire with outstanding braking performance on all road surfaces is required since the road surface conditions constantly change in this manner.

Various rubber compositions for the treads have been proposed to cope with such safety demands. For example, oil expanded natural rubber has been reported as rubber with outstanding braking performance on icy surfaces [K.A. Grosch, A. Sahailamach, K. Southern, P. McL Swift: Tennen Gomu (Natural Rubber) (1970), 2 359]. However, oil expanded natural rubber has inferior braking performance in comparison to polybutadiene rubber on icy surfaces, especially on extremely cold surfaces at -25°C. The braking performance on wet surfaces deteriorates when polybutadiene rubber is admixed to improve the braking performance on icy surfaces. Furthermore, the braking performance on icy surfaces declines when large amounts of styrene butadiene copolymer rubber are blended or when the carbon black content is raised to improve the braking performance on wet surfaces.

Methods in which part or all of the carbon black is replaced by active silicate (Patent Disclosure No. 88150-1975) or by polyisobutylene (Patent Disclosure No. 546-1976) have been presented as methods of improving both the braking performance on wet surfaces and the braking performance on key surfaces. However, neither

method provides adequate effects. A tire which provides high levels of braking performance on both wet surfaces and on ky surfaces has not been obtained yet.

This invention eliminates the aforementioned problems. The object is to provide a rubber composition for tire tread having outstanding braking performance on both wet surfaces and icy surfaces. In particular, it is ideal for the tread of steel belted tires used on passenger cars.

The inventors have conducted various studies to attained the aforementioned object in order to produce a rubber composition for tire treads having outstanding braking performance on both wet surfaces and icy surfaces, and have focused on utilization of the fact that the friction mechanism differs on various surfaces. The rubber composition undergoes deformation due to the ice crystals or the irregular surface to produce heat, and both the resulting loss component and the energy loss attributable to the adhesion between the rubber composition and the key surfaces contribute to the friction resistance of rubber compositions on key surfaces. The modulus of elasticity of rubber compositions rapidly increases in low-temperature regions of 0°C or less. and the contribution of both components diminishes as a result. On the other hand, the contribution to the friction resistance of the rubber composition on wet surfaces of the energy loss attributable to the adhesion between the road surface and the rubber composition is slight because of an ice film which is present between the surface and the rubber composition, and the adhesion is attributable primarily to the energy loss during deformation of the rubber composition. Specifically, the energy loss of the rubber composition during deformation at low temperatures must be increased and the modulus of elasticity of the rubber composition at low temperatures must be increased, thereby increasing the contact area with the icy surface, to improve the friction resistance of a rubber composition on both icy surfaces and wet surfaces concurrently. The glass transition temperature of a rubber composition shifts to the high-temperature side when the energy loss in usual rubber compositions increases during deformation at low temperatures, and the modulus of elasticity rises at low temperatures.

Thus, the inventors have conducted thorough research to eliminate those problems, the results of which have culminated in the discovery of the following important findings. Specifically, the energy loss during deformation of a rubber composition is caused by factors attributable to the interaction between carbon black and raw material rubber rather than factors attributable only to the raw material rubber. As a result, if carbon black and expansion oil are suitably selected and if large amounts are blended, the factors attributable to said interaction would increase, and it would be possible to reduce the modulus of elasticity of the rubber composition at low temperatures. This invention is based on the aforementioned findings.

Specifically, this invention concerns a rubber composition for tire treads comprising 10-50 weight parts of natural rubber and/or synthetic polyisoprene rubber and 50-90 weight parts of polyisoprene rubber with a polybutadiene rubber content of 50 wt% or more in which the content of trans 1-4 bonds is 30 wt% or more and the content of vinyl bonds is 10% or less, said composition characterized by the fact that 20-200 weight parts of carbon black are blended per 100 weight parts of said rubber and by the fact that the relation between the amount of dibutyl phthalate oil absorption x (ml/100 g) and the amount of iodine adhesion y (mg/g) by said carbon black satisfies relations Ω - Ω below

Both natural rubber (NR) and/or synthetic polyisoburylene rubber (IR) as well as polybutadiene rubber (specific BR) with specific trans 1,4 and vinyl bonds are used as the raw material rubber ingredient in the rubber composition for tire treads of this invention. The specific BR used in this invention is BR in which the vinyl bond content is 10% or less to improve the braking performance of tires on icy surfaces while the trans 1,4-bond content is 30% or more to improve the braking performance on wet surfaces. The ice skid resistance, which is an indicator of the braking performance on icy surfaces, declines if the vinyl bond content of this BR should exceed 10%, while the wet skid resistance, which is an indicator of the braking performance on wet

surfaces, declines if the trans 1,4-bond content should fall below 30%. Furthermore, the ice skid resistance is the friction resistance of the rubber composition on an icy surface when the temperature of the ice and rubber test specimens is set at -25°C using a British portable skid tester. In addition, the wet skid resistance is the friction resistance of the rubber composition on a wet surface when the temperature of the rubber test specimens and the pavement which has been moistened with distilled water using a skid tester similarly is set at -25°C using a skid tester. The wet surfaces used in wet skid measurements are type B safety walks for outdoor use made by 3M Co. The braking performance of tires on icy surfaces can be improved if the ice skid resistance is increased, and the braking performance of tires on wet surfaces could be improved if the wet skid resistance is increased.

The blending proportions of BR and NR (IR), the raw material rubber ingredient, in the rubber composition of this invention should be in the range of 10-50 weight parts of NR (IR) and 50-90 weight parts of BR per 100 weight parts of raw material rubber ingredient. The balance between the ice skid resistance and the wet skid resistance is outstanding in this range. The wet skid resistance declines if the amount of NR (IR) which is blended should fall below 10 weight parts while the ice skid resistance declines if it should exceed 50 weight parts, both of which are undesirable. Furthermore, it is essential that the content of specific BR in the BR be 50 wt% or more. A good balance between the ice skid resistance and the wet skid resistance is lost if the content of specific BR in the BR falls below 50 wt%.

The carbon black which is blended in the rubber composition for tire treads pursuant to this invention is the type which has a low level of reinforcing properties. Carbon black N 339 or carbon black N 347 with an especially small particle size are used even in intermediate super abrasion furnace (abbreviated ISAF) or high abrasion furnace (abbreviated HAF) in consideration of the wear resistance in the tire tread section of pneumatic tires. However, such carbon blacks have poor braking performance on icy surfaces in comparison to the carbon black used in this invention and are undestrable.

The carbon black used in this invention is carbon black with comparatively low reinforcing properties. The relation between the amount of DBP oil absorption x (mi/100 g) and the amount of iodine adhesion y (mg/g) by the carbon black must satisfy relations $\mathbb{O} - \mathbb{O}$ below

This range is the range represented by the slanted lines in Figure 1. Carbon black N 326, N 334, N 550 and N 660 are relevant examples of the carbon black in this range. The ice skid resistance declines, which is undestrable, when the iodine adhesion amount and the DBP oil absorption amount are in the range of y > x + 170, specifically when the range is to the upper right of the slanted-line region. The wear resistance declines, which is undestrable, if the iodine adhesion amount and the DBP oil absorption amount have the relationship y < x + 110, specifically if the range is to the lower left of the shaded region. The iodine adhesion amount (m/100 g) and the DBP oil absorption amount (mi/100 g) are both measured by the method presented in JIS K 6221.

A total of 20-200 weight parts of carbon black are blended per 100 weight parts of raw material rubber ingredient in the rubber composition for tire treads pursuant to this invention. It becomes difficult to attain satisfactory ice skid resistance and wet skid resistance if the amount blended falls below 20 weight parts, while the blending operational efficiency deteriorates, which is undesirable, if it exceeds 200 weight parts.

The rubber composition for tire treads pursuant to this invention may contain suitable, arbitrary amounts of extending oil, sulfur, vulcanization accelerator, and various types of antioxidants including anti-heat-resistance agent, anti-ozone-resistance agent and anti-flexion resistance agent in addition to the aforementioned carbon black.

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1: Diene NF 35R (36% cis.1,4 bond content, 54% trans 1,4-bond content, 10% vinyl bond content, Asahi Chemical Industry Co. Ltd.)
2: Nipol BR 1220 (98% cis.1,4 bond content, 1% trans 1,4-bond content, 1% vinyl bond content, Nihon Zeon Co., Ltd.)
3: High vinyl butadiene tubber (20% cis.1,4 bond content, 30% trans 1,4-bond content, 50% vinyl bond content, Nihon Zeon Co., Ltd.)

This invention is explained concretely below through actual examples and comparative examples. The blended am unts in Table 1 are all based on weight parts.

Examples 1-5 and Comparative Examples 1-10

Raw material rubber ingredient and various types of blended agents were blended at the proportions illustrated in Table 1, mixed, and rubber compositions were prepared. The amount of iodine adhesion to the various types of carbon black used and the amount of DBP oil absorption are presented in Table 2 and Figure 1.

The ice skid resistance, wet skid resistance and pico abrasion of the vulcanized rubber obtained upon vulcanization of the rubber composition for 15 minutes at 160°C were measured, and the results are illustrated in Table 1. In addition, the ice skid resistance of examples 1-2 and comparative examples 1-4 as well as the wet skid resistance are presented in Figure 2. The ice skid resistance and the wet skid resistance were measured using a British portable skid tester, as mentioned above. The amount of pico abrasion was the amount of pico abrasion decrease measured by a Goodrich type pico abrasion tester.

Table 2

Number	Carbon black	Iodine adhesion	DBP oil absorption amount
Φ	Carbon black N 220	118	114
•	Carbon black N 339	90,	110
٥	Carbon black N 351	67	120
•	Carbon black N 330	80	102
•	Carbon black N 334	65	100
•	Carbon black N 326	86	73
ð	Carbon black N 550	40	118
•	Carbon black N 660	34	90

The amounts of NR and specific BR which were used as the raw material rubber ingredient in examples 1-2 and comparative examples 1-4 in Table 1 were altered, and carbon black N 334 was used as the carbon black. Comparative examples 1 in which NR was used alone as the raw material rubber ingredient exhibited high wet skid resistance values, but the ice skid resistance was low, there was a large amount of pico abrasion, and the wear resistance also was poor. Examples 1-2 and comparative examples 2-3 which combined NR and specific BR exhibited improvement in the loe skid resistance as the amount of specific BR increased, in contrast to comparative example 1 in which NR was used alone as the raw material rubber ingredient, and the amount of pico abrasion was also slight. However, although the ice skid resistance and the wear resistance were outstanding in comparative example 4, in which specific BR was used alone as the raw material rubber ingredient, the wet skid resistance fell. Figure 2 illustrates a graph which plots the values of the ice skid resistance and the wet skid resistance in examples 1-2 and comparative examples 1-4 in which the amounts of NR and of specific BR had been altered. Figure 2 clearly indicates that the blend of rubber which exhibits a good balance between the ice skid resistance and the wet skid resistance contains 10-50 weight parts of NR and 50-90 weight parts of specific BR per 100 weight parts of raw material rubber ingredient.

Comparative examples 5-6 use BR other than specific BR as the raw material rubber ingredient. Specifically, they combine NR with BR which does not meet the requisites since the trans 1,4-bond content exceeds 30% and the vinyl bond content is 10% or less. Although carbon black N 334, which was used in example 1, is applied here as the raw material rubber ingredient, the wet skid resistance was somewhat lower than that in which BR-1 was used. Furthermore, ice skid resistance and the wear resistance were inferior to those in comparative example 6 which used V-BR.

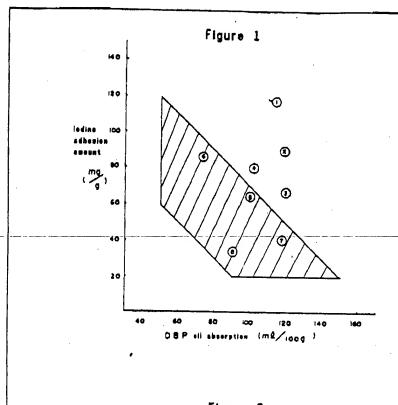
Examples 3-5 and comparative examples 7-10 used NR, specific BR and BR-1 as the raw material rubber ingredient with varied types of carbon black used. Examples 3-5, in which the carbon black of this invention was blended, exhibited a better balance between the wet skid resistance and the ice skid resistance than comparative examples 7-10 in which carbon black outside of the range of the invention was blended, and the wear resistance was also in the permissible range.

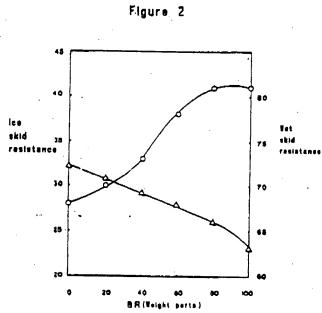
As explained above, the rubber composition for tire treads pursuant to this invention in which polybutadiene rubber comprising primarily natural rubber and/or synthetic polyisoprene rubber and specific polybutadiene rubber is the raw material rubber ingredient and in which carbon black with specific properties is blended has outstanding braking performance on both icy surfaces and wet surfaces. Moreover, the rubber composition can be applied ideally as tread material for pneumatic tires since the wear resistance is within the allowable range, and it can also be used as the tread material for snow tires and studded tires which are used in extremely cold regions. It can also be applied in products other than tires in which the characteristics of great abrasion resistance with ice are required, such as the track belts for snowmobiles and solid tires.

4. Brief Description of Drawings

Figure 1 is a graph illustrating the range of the iodine adhesion and the DBP oil absorption amount of the carbon black used in this invention.

Figure 2 is a graph illustrating the changes in the ice skid resistance and in the wet skid resistance for blending ratios of NR and specific BR. These correspond to examples 1-2 and comparative examples 1-4.





translation 5834

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54 Pneumatic tire

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Specification

1. Title of Invention

Pneumatic tire.

2. Scope of Patent Claim

A pneumatic tire in which the tread rubber is blended rubber consisting of 5-200 weight parts of at least one type of diene based rubber (B) selected from the group comprising natural rubber, polysisoprene rubber, styrene-butadiene rubber or cis-1,4-polybutadiene rubber to 100 weight parts of (A), polybutadiene with 60-90 wt.% of trans-1,4-bonds and no more than 10 wt.% of 1,2-bonds, said tire characterized by the fact that the groove area ratio of the tread section to the entire contact area is 30-50%.

3. Detailed Description of the Invention

|Fleid of Industrial Utilization|

This invention concerns a pneumatic tire with outstanding braking performance on wet roads at high speeds and chipping resistance. Specifically, it concerns a pneumatic tire for passenger cars.

[Conventional Techniques]

The performance of vehicles has improved in recent years, and the use of special high performance vehicles or four-wheel drive vehicles has spread.

High braking performance on wet roads at high speeds and high chipping resistance of tires has been called for in such vehicles.

The use of tread rubber combining styrene-butadiene capolymer rubber with a high styrene content and butyl rubber has been practiced as means of improving the braking performance on wet roads (Patent Publication No. 14581-1969).

However, the tread blending such rubber has had the problem of reduction of braking performance on icy roads in the winter.

Moreover, the method of arranging water discharge grooves in the circumferential direction of the tire tread using tread rubber with low heating properties and inferior braking performance on wet roads has also been practiced (Patent Disclosure No. 69101-1977, Patent Publication No. 18248-1983).

Accordingly, the tread pattern would be a block shape, and the tread rubber when contact is made would be prone to deformation.

In addition, compositions blending specific carbon black in blended rubber with trans-1,d-polybutadiene and cis-1,4-polyisoprene have been used in tread rubber (Patent Disclosure No. 133036-1985). While such rubber compositions have outstanding braking performance on icy roads, the braking performance on wet roads in pneumatic tires with great groove areas in the tread pattern has been inferior, which is a problem.

[Objective of Invention]

The objective of this invention is to provide a been with outstanding braking performance and chipping resistance on wet roads at high speeds, thereby eliminating the aforementioned defects of conventional technology.



[Composition of Invention]

The pneumatic tire of this invention which attains the aforementioned objectives is one in which the trend rubber is blended rubber consisting of 5-200 weight parts of at least one type of diene based rubber (B) selected from the group comprising natural rubber, polyisoprene rubber, styrene-butadiene rubber or cis-1,4-polybutadiene rubber to 100 weight parts of (A), polybutadiene with 60-90 wt.% of trans-1,4-bonds and no more than 10 wt.% of 1,2-bonds. This tire is characterized by the fact that the groove area ratio of the tread section to the entire contact area is 30-50%.

This invention is explained in detail below.

The polybutadiene (A) used in this invention must have 60-90 wt.% of trans-1.4 bonds and no more than 10 wt.% of 1,2 bonds (vinyl bonds).

The cut-chipping resistance is reduced when the amount of trans-1.4 bonds falls below 60 wt.%, while production becomes extremely difficult when the amount of trans-1.4-polybutadiene exceeds 90 wt.%, and this is uneconomical. The most desirable range is 70-80 wt.%

In addition, the rubber itself becomes prone to heating when the amount of 1,2-bonds exceeds 10 wt.%. Thus, a level of no more than 8 wt.% is desirable.

The polybutadiene (A) can be preduced by solution polymerization of butadiene in the presence of a compound catalyst such as Ba compound/organic Li compound. Emulsion polymerization would also be possible, but alteration of the microstructure of the butadiene section is difficult in emulsion polymerization, and it is difficult to hold the amount of 1,2-bonds (vinyl bonds) below 10 wt.%. Thus, this method is undesirable.

The diene-based rubber (B) used in this invention is selected from the group comprising natural rubber, polyisoprene rubber, styrene-butadiene rubber, cis-1,4-polybutadiene and high styrene-butadiene rubber.

The blending ratio of polybutadiene (A) to diene-based rubber (B) in this invention must be 5-2000 weight parts of diene-based rubber (B) to 100 weight parts of polybutadiene (A). The braking performance on wet roads and the improvement in chipping resistance are too low when tess than 5 weight parts of diene-based rubber (B) are used. Thus, the objectives of this invention are not attained.

This invention uses the aforementioned blended rubber as the tread rubber, and a pattern must be formed in which the groove area ratio of the tread section of the tire to the entire contact area is 30~50%. The groove area and the contact area of the tread section are measured pursuant to JIS using the contact shape with standard pneumatic pressure and standard load. The ratio of the contact area to the groove area is then determined.

The braking performance at high speeds on wet roads is reduced when the groove area ratio falls below 30%, and the tire cannot perform as a high performance tire, as a tire for four-wheel drive vehicles or as an all-season tire. Moreover, the contact pressure of the tread surface becomes too great when the groove area ratio exceeds 50%, and the abrasion life of the tire is reduced, which is impractical.

This invention is explained concretely below through actual examples.

Polybutadiene with two types of microstructure was used, as illustrated in Table 1 below.

Table I

Type of polybutadiene	BR-1	BR-2	
Cis-1.4 bond weight (%) Trans-1.4-bond weight (%) 1,3-bond (vinyl) bond weight (%)	94 1 1	16.1 70.8 4.7	

The microstructure of the butadiene section was measured by IR.

In addition, the BR-1 v as "Nipol" 1220 (product of Nihon Zeon Co.).

Using the polybutadiene BR-1 and BR-2 of Table 1, 30 weight parts of polybutadiene, 70 weight parts of styrene-butadiene copolymer rubber, 70 weight parts of HAF-11S carbon black, 2 weight parts of stearic acid, 40 weight parts of aromatic oil, 2 weight parts of sulfur and 1.2 weight parts of vulcanization accelerator OBS were blended using a Bumbury's mixer and open roll. This was used to produce the tread rubber of a 195/60tR14 tire illustrated in Table 2 below. The chipping resistance test results are also illustrated. The chipping resistance was evaluated after observing the mode of rubber disintegration of the tread surface.

Table :

Tire	T·1	T-2	T·S
	Comp. Est. 1	Comp. Es. 2	Comp. Ex. 3
Groove area ratio (%) Styrens-butadiene copplymer rubber (phr) BR-1 (phr) BR-2 (phr) Chipping resistance	30	40	40
	70	70	70
	30	30	0
	0	0	30
	Good	Pmor	Good

A wet road was created by sprinkling water on a test course of the Japan Automobile Road Research Center, and the coefficients of friction of tires T-1, T-2 and T-3 illustrated in Table 2 were measured at speeds of 20-80 km/h. Figure 1 illustrates the results.

The results of Tables I and 2 and of Figure I reveal the following.

The tire T-1 (Comparative Example 1) uses polybutadiene in which the trans-1,4-bond amount is very low, at 1%, and the groove area ratio is only 20%. As a result, the coefficient of friction on wet roads, especially the braking performance at high speeds, is poor although the chipping resistance is good.

Tire T-2 (Comparative Example 2) also uses polybutadiene in which the trans-1,4-bond weight is low, and the groove area ratio has been improved to 40%, but the chipping resistance remains poor and the coefficient of friction on wet roads is poor at low speeds.

In contrast, tire T-3 (Actual Example) uses polybutadiene in which the trans-1,4-bond weight is 70.2 wt.%. The chipping resistance is good since the groove area ratio has been set at 40%, and the coefficient of friction on wet roads is also increased, especially at high speeds.

Effects of Invention

This invention provides outstanding chipping resistance and high speed braking performance on wet roads in a tire which uses blended rubber comprising polybutadiene with a high trans-1,4-bond amount and diene-based rubber in the tread section, a tire in which a specific groove area ratio has been set.

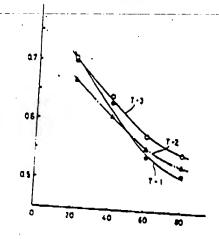
4. Brief Description of Drawings

Figure 1 is a graph illustrating the relation between the running speed of a tire and the coefficient of friction on a wet road.

T-1.. tire of Comparative Example 1, T-2.. tire of Comparative Example 2, T-3.. tire of Actual Example.

Figure 1

Coefficient of friction



Speed [Km/h]